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(54) IN-SERVICE CLEANING OF WATER SYSTEMS

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the in-service cleaning of water systems and in particular to two-stage method of in-service cleaning of a water system having each of (1) iron oxide, and (2) hardness, i.e. carbonates and/or phosphates of calcium, and/or magnesium, deposited on the interior metal surface thereof.

In the cleaning of water systems it has been common practice to take the system out of service and to remove harness and iron oxide deposits by conventional methods such as soaking with and/or circulating aqueous mineral acid solutions or an aqueous alkaline solution of an amino polycarboxylic acid such as ethylene diamine tetraacetic acid (EDTA). These methods suffer from the disadvantage that the cooling water system is generally not taken out of service until heat exchange capacity becomes very poor and this often happens just at a time that is most inconvenient for the operator, for example, during the height of a busy season.

In-service cleaning also has been attempted using an aqueous alkaline solution of an amino polyacetic acid as cleaning solution but this has not been very successful since iron oxide removal is very poor unless temperatures above 200°F are employed.

It has now been discovered and the discovery forms the basis for the present invention that scale deposits containing iron oxide and hardness on the water side surfaces of flowing water systems e.g. a recirculating water cooling system can now be efficiently and effectively removed while the system remains in service by adding one or more aminocarboxylate chelating agents to the water in a proportion to dissolve a substantial portion of the scale.

In accordance with the present invention there is provided a process for the removal of scale deposits containing iron oxide and hardness as hereinbefore defined from the water-side surfaces of a flowing water system which process comprises adding one or more aminocarboxylate chelating agents to the water in a proportion to dissolve substantially all of the scale, wherein substantially all of the hardness scale is removed by a first stage treatment in which the chelating agent and as required sufficient of a water soluble base is added to the water to provide a solution of from 7 pH to 12 pH and the alkaline solution is circulated for a period of time to bring the chelation reaction substantially to completion and substantially all of the iron oxide is removed by a second stage treatment in which an acidifying agent is added to the water in a proportion to provide a solution of 3 to 6 pH additional chelating agent being added as required, and the acidic solution is circulated for a period of time to bring the reaction of the solution with the iron oxide substantially to completion.

As preferred embodiments substantially all of the water in the system is displaced with make-up water prior to the first stage treatment; substantially all of the spent first stage treatment solution is displaced with make-up water prior to the second stage treatment; the first stage treatment solution is adjusted to 8 to 11 pH and the second stage treatment solution is adjusted to 4.0 to 5.5 pH. Acidifying agents suitable for use in the second stage treatment solution include sulfuric acid, formic acid, aminopolycarboxylic acids and di-, tri, or poly-carboxylic acids of from 2 to 8 carbon atoms such as, for example, citric acid, tartaric acid or acetic acid. It is desirable to employ a corrosion

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inhibitor in the second stage of treatment and usually the normal water treatment is discontinued during both stages of treatment.

Particularly good results are obtained and corrosion is substantially reduced by the presence in the second stage acidic solution of 0.05 to 1 weight percent of a corrosion inhibitor comprising 1 to 9 parts by weight of an organic sulfur compound having sulfur present in the form of —S— or S= and 9 to 1 parts by weight of an adduct obtained by reacting at 150 to 250°F one mole of an ammonium derivative having at least one hydrogen atom bonded to a nitrogen atom and no other reactive substituents with 1.5 to 10 moles of a ketone having at least one hydrogen bonded to the carbon atom adjacent to the carbonyl group, 2 to 10 moles of an aldehyde selected from 1 to 16 carbon aliphatic aldehydes and aromatic aldehydes having no other reactive substituents and 0.3 to 24 parts by weight for each part by weight of the sum of the weights of the ammonium derivative, ketone and aldehyde of a 1 to 20 carbon fatty acid.

Advantageously, the organic sulfur compound is an N - alkylthiourea, the ammonium derivative is dehydroabiethylamine, the ketone is acetophenone, the aldehyde is paraformaldehyde and the acid is formic acid.

The present method is applicable to in-service cleaning of most circulating cooling water systems, for example, an open system used in connection with an air-conditioning system where displacement of circulating aqueous liquid is economically feasible so that two-stage cleaning is possible as a practical matter, and where removal of both iron oxide and hardness is an important objective.

The acidifying agent employed in the second stage may be almost an proton-donating substance which provides a substantial concentration of hydrogen ions in aqueous solution sufficient to provide the pH value desired in the range of 3 to 6. Such proton-donating substance preferably does not form a precipitate, nor not more than a slight amount of easily suspended precipitate, with dissolved salts or dissolved deposits at the concentrations found in the circulating system and is, therefore, compatible with the system.

Almost any mineral acid may be used, but sulfuric acid is most preferred of these since chloride or nitrate ions may be harmful to the system. Also suitable are the organic i.e. carboxylic acids. These include the di-, tri- or poly-carboxylic acids containing from 2 to 8 carbon atoms, including the hydroxy polycarboxylic acids all of which are appropriately described as complexing agents. Suitable polycarboxylic acids include citric acid, tartaric acid, oxalocitraconic acid, oxalic acid, malonic acid, succinic acid, malic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, diglycolic acid and phthalic acid. Of these, citric acid and tartaric acid are preferred. In general, however, it is simple and inexpensive and quite adequate to employ the lower molecular weight monocarboxylic acids such as those containing less than seven carbon atoms, e.g., formic acid, and acetic acid.

In addition, the chelant itself may be used in free acid form, obviating the need for any other acid. In this case, however, it is generally advisable to use both the acid form and the ammonium salt of the chelating agent together.

Suitable amino carboxylic acid chelating agents for use in the practice of the present invention include the aminocarboxylic acids of the formula

$$(HOOCCH_2)_2N[(CH_2)_nN(CH_2COOH)]_mCH_2COOH,$$

wherein n is an integer from 1 to 4 inclusive and m is a numeral in the range of 0 to 4 inclusive and wherein up to two of the carboxymethyl groups may be replaced with a β-hydroxyethyl group and one or more of the carboxymethyl broups may be replaced by carboxyethyl groups. Specific examples of such acids which are particularly suitable are ethylene diaminetetraacetic acid (EDTA), N-hydroxymethyl ethylenediaminetriacetic acid, nitrilotriacetic acid, N - 2 - hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid and mixtures thereof.

Any of these amino carboxylic acid chelating agents or a mixture thereof, are suitably employed, in the first stage cleaning, in the form of one of their alkali metal or ammonium salts, normally the sodium salt, and preferably the fully neutralized salt since it imparts the greatest alkalinity.

Any of these same amino carboxylic acid chelating agents, or a mixture thereof, are suitably employed in the second stage cleaning in the form of the fully neutralized salt, unless the free acid or partially neutralized form is used to obtain the desired acidity.

The amino carboxylic acid chelating agents are conveniently employed in the form of an aqueous solution in which they are normally supplied commercially, typically, a 38 percent by weight aqueous solution.

A corrosion inhibitor is generally not needed during the first stage cleaning unless the cooling system contains or is suspected to contain copper or copper bearing portions

in contact with the circulating liquid. In that event an inhibitor such as sodium mercaptobenzothiazole is preferably employed at a concentration of 0.1 to 0.5 percent by weight.

In most instances, it is preferred to employ an inhibitor to completely eliminate and thus reduce still further the relatively low level attack upon the metal substrate that occurs when using the present cleaning solution in the second stage. A suitable inhibitor used at a concentration of 0.05 to 1 percent by weight is a commerical product compounded in a formulation that includes polyethoxylated fatty acids and similar materials, and is more thoroughly described in Chemical Abstracts, Volume 62, Column 7448d (1965).

In carrying out the method of the invention, normal water treatment to the circulating cooling water system is discontinued during cleaning operations. It is highly advisable to blow down the system sufficiently to reduce the concentration of dissolved salts in the system to the equivalent of one to one and one-half cycles of operation in order to avoid undue consumption of chelating materials. The amino carboxylic acid chelating agent in the form of its sodium or ammonium salt and conveniently in relatively concentrated aqueous solution, i.e., greater than about 20 percent by weight concentration, and typically, 38 percent by weight, is injected into the circulating system at any convenient point. Usually a convenient point of injection is the main feed pump. Sufficient chelating agent is injected to dissolve and complex the amount of hardness estimated to be in the system. Generally about 3.8 parts by weight of chelating agent, on a dry basis, is needed per part weight of hardness deposits to be dissolved. Ordinarily the pH of the circulating system prior to cleaning exhibits a value of about 6.5 to 7.2, i.e., approximately neutral. Addition of the chelating agent in the form of the fully neutralized sodium salt normally brings the pH of the system to a value in the range of 7 to 12. If the pH is lower than 8, however, it is preferred to adjust the pH upward to the range of pH 8—11, and more preferably to pH 10—11, by the addition of alkaline material, preferably caustic soda.

The solution of chelating agent is usually allowed to circulate for several hours or sometimes a day or more, or until successive samples of the system taken at least 15 minutes apart and examined by chemical analysis show that there is some unspent chelating agent in the system and the degree of spentness does not change during the time between samples. If the chelating agent is entirely spent or is substantially entirely spent and the degree of spentness is still increasing, an additional quantity of chelating agent in the form of the sodium salt is preferably injected in order to complete the removal of hardness, and circulation of the cleaning solution is desirably continued until substantially complete removal of hardness has been indicated, as by additional sampling and analysis for unspent chelating agent.

When removal of hardness has been satisfactorily concluded, the cleaning solution is ordinarily displaced gradually and as rapidly as facilities permit by the addition of make-up water and concurrent blow down of a corresponding amount of circulating liquid. Sufficient displacement should be carried out to remove enough of the spent cleaning solution to bring the pH of the circulating system back to approximately the pH of the make-up water, i.e., approximate neutrality, so that acid requirements are reduced in the second stage, and also so that dissolved and chelated calcium ion does not become dissociated and precipitated when the pH is lowered below pH 5.

In the second stage of cleaning, amino carboxylic acid chelating agent, preferably as the ammonium salt, though the alkali metal salt may be used, and, an acidifying agent are added to the system with or without prior mixing in a manner similar to the injection of chelating agent during the first stage. The material added by injection must bring the pH of the system down to a value in the range of 3 to 6, and more preferably to a pH of 4 to 5.5. The quantity of mixture of acidifying agent and chelating agent is an amount calculated to be sufficient to dissolve and complex or chelate the iron in the iron oxide deposits in the system. Generally 1.9 parts by weight of a complexing agent such as the nitrogen-free polycarboxylic acids described, or 3.8 parts by weight of chelating agent, on a dry basis, are each sufficient to dissolve and tie up one part by weight of iron oxide.

Again the so-prepared acidic cleaning solution is circulated for several hours, or sometimes a day or more, or until successive samples drawn from the system at intervals at least 15 minutes apart indicate that dissolution of iron oxide is substantially complete.

If the cleaning materials are entirely spent or if they are substantially entirely spent and analysis indicates iron oxide is still being taken up, one or more small additions of the mixture of acidifying agent and chelating agent are made, if desired, to complete removal of iron oxide.

The cleaning operation is completed upon displacing the cleaning solution from the circulating system by addition of make-up water whereby the pH of the circulating system is brought back to a normal operating value close to pH 7.

As indicated above, if desired, a corrosion inhibitor is employed in each stage of the cleaning. Such corrosion inhibitor is con-

veniently dissolved in the aqueous solution of chelating agent prior to injection.

In another, more simplified, embodiment of the invention, the cleaning solution is not displaced after first stage treatment to dissolve hardness but second stage cleaning is commenced simply by dropping the pH with an acidifying agent and adding additional chelating agent, preferably as the ammonium salt or the alkali metal salt, or as the free amino carboxylic acid. If the calcium concentration is substantial, as from the removal of heavy deposits of hardness, care must be taken to avoid a pH below 5, since calcium chelate tends to dissociate and calcium may percipitate from solution under these conditions.

Because of the narrowness of the range of suitable pH values in the presence of calcium, the simplified method is of greatest advantage when systems are not so heavily coated with hardness, e.g., when they are cleaned frequently, so that lower pH values may be readily tolerated without displacing calcium chelate from the system until iron oxide removal is completed.

Example 1

An open-recirculating cooling water system containing heat exchange equipment holds 84,000 gallons (318 m^3) of water with a recirculation rate of 24,000 gallons (91 m^3) per minute. The make-up rate of water is 1100 to 1200 gallons (4.17 to 4.54 m^3) per minute. The system contains both iron and calcium-bearing deposits primarily in the forms of Fe_2O_3 and $Ca_{10}(OH)_2(PO_4)_6$. The total estimated scale is 11,781 pounds (5.34 tonne) with 7,028 pounds (3.19 tonne) of $Ca_{10}(OH)_2(PO_4)_6$ and 4,753 pounds (2.15 tonne) of Fe_2O_3.Total estimated material requirements to dissolve this scale in two stages is: 66,903 pounds (30.3 tonne) of 38% aqueous solution of tetra ammonium EDTA, 47,530 pounds (21.5 tonne) of aqueous solution of tetra ammonium EDTA (38% by weight concentration of EDTA), 8,802 pounds (4 tonne) of anhydrous citric acid, and 84 gallons (318 l) of inhibitor.

Prior to any chemical injection, the cooling tower is blown down to establish one to one and one half cycles of concentration of dissolved mineral content. The system exhibits a pH of 6.8. At the start of the first stage of cleaning the aqueous solution of inhibited tetra sodium EDTA is steadily injected into the system through a convenient point in the circulating system just ahead of the pump. The pH is adjusted to the preferred range of 10—11 by caustic soda. The chelating material circulates througout the system until hardness tests show it has stopped spending, i.e., has stopped dissolving and complexing hardness.

This solution is then removed from the system by periodic displacement using the system's make-up water supply. This step is completed when the pH of the circulating water is that of the make-up water, i.e., about 7.

In the second stage of cleaning, the tetra ammonium EDTA, citric acid, and inhibitor are mixed and added to the system in the same manner as the tetrasodium EDTA was added. The inhibitor consists of a mixture of (1) nonyl phenol condensed with 20 moles of ethylene oxide, (2) 1-hexyn-3-ol, (3) 1-alkyl-2-thiourea, and (4) the reaction product of dehydrobietylamine, paraformaldehyde, formic acid, and acetophenone. The material added by injection brings the pH to 5.6. This material circulates until spending has ceased, as shown by analysis, indicating that iron oxide is substantially all dissolved.

The second stage cleaning solution is then removed from the system by steady displacement using the system make-up water supply. The cleaning operation is completed when the pH of the circulating water again becomes that of make-up water, i.e., 6.8

The cooling water system is successfully cleaned while in service by the foregoing recited steps as shown by the temperature of water returning from the cooling tower being below 90°F. (32°C.). Further, operating experience after cleaning shows subsequent cleaning is not needed again until 5 months later.

Example 2

The method of Example 1 is repeated on a similar cooling water system except that the amount of hardness and scale are not greater than estimated, as shown by analysis for the spentness of the chelating material at each stage, indicating that chelant is entirely spent.

The remaining hardness is removed during the first stage by the injection, dissolution and circulation of an additional 8,500 pounds (3.86 tonne) of 38 percent aqueous solution of tetra sodium EDTA before displacement of cleaning solution. During the second stage, there is added an additional 4,750 pounds (2.15 tonne) of aqueous solution of tetra ammonium EDTA (38 percent by weight concentration of EDTA salt), 880 pounds (440 kg) of anhydrous citric acid, and 8.4 gallons (31.8 l) of inhibitor, to complete the take-up of iron oxide before displacement of cleaning solution. The same excellent cleaning results are obtained as in Example 1.

Using (1) the sodium salt of any nitrilotriacetic acid, N-hydroxy-ethyl ethylenediaminetriacetic acid, N-2-hydroxyethyliminodiacetic acid, or diethylenetriamenepentaacetic acid in place of tetrasodium EDTA; (2) the ammonium salt of such chelants in place of tetra-ammonium EDTA; and (3)

oxalic acid, malonic acid, tartaric acid, formic acid, acetic acid, or sulfuric acid in place of citric acid, in Examples 1 or 2, similar eminently satisfactory cleaning results are obtained.

WHAT WE CLAIM IS:—

1. A process for the removal of scale deposits containing iron oxide and hardness as hereinbefore defined from the water-side surfaces of a flowing water system which process comprises adding one or more amino carboxylate chelating agents to the water in a proportion to dissolve substantially all of the scale, wherein substantially all of the hardness scale is removed by a first stage treatment in which the chelating agent and as required sufficient of a water soluble base is added to the water to provide a solution of from 7 pH to 12 pH and the alkaline solution is circulated for a period of time to bring the chelation reaction substantially to completion and substantially all of the iron oxide is removed by a second stage treatment in which an acidifying agent is added to the water in a proportion to provide a solution of 3 to 6 pH additional chelating agent being added as required, and the acidic solution is circulated for a period of time to bring the reaction of the solution with the iron oxide substantially to completion.

2. A process as claimed in claim 1 wherein the water in the system is substantially all displaced with make-up water prior to the first stage treatment.

3. A process as claimed in claim 1 or 2 wherein the alkaline solution of the first stage treatment is substantially all displaced with make-up water prior to the second stage treatment.

4. A process as claimed in any of claims 1 to 3 wherein the soluble base is added in a proportion to provide a first stage solution of 8 to 11 pH.

5. A process as claimed in any of claims 1 to 4 wherein the soluble base is added in a proportion to provide a first stage solution of 10 to 11 pH.

6. A process as claimed in any of claims 1 to 5 wherein the soluble base is caustic soda.

7. A process as claimed in any of claims 1 to 6 wherein the acidifying agent is added in a proportion to provide a second stage solution of 4.0 to 5.5 pH.

8. A process as claimed in any of claims 1 to 7 wherein sulfuric acid, one or more di-, tri-, or poly-carboxylic acids having 2 to 8 carbon atoms or aminopolycarboxylic acids are added to acidify the second stage solution.

9. A process as claimed in any of claims 1 to 7 wherein citric acid, tartaric acid, acetic acid or formic acid or a combination of two or more thereof is added to acidify the second stage solution.

10. A process as claimed in any of claims 1 to 9 wherein the chelating agent employed is selected from alkali metal- or ammonium salts of aminocarboxylic acids.

11. A process as claimed in any of claims 1 to 10 wherein the chelating agent employed is selected from alkali metal- or ammonium salts of aminocarboxylic acids of the formula

$$(HOOCCH_2)_2N[(CH_2)_nN(CH_2COOH)]_m\ CH_2COOH,$$

wherein n is an integer from 1 to 4 inclusive and m is a numeral in the range of 0 to 4 inclusive and wherein up to two of the carboxymethyl groups may be replaced with a β-hydroxyethyl group and one or more of the carboxymethyl groups may be replaced by carboxymethyl groups.

12. A process as claimed in any of claims 1 to 11 wherein a corrosion inhibitor is added to the acidic second stage treatment solution.

13. A process as claimed in any of claims 1 to 11 wherein corrosion in the system is substantially reduced by the presence in the acidic second stage treatment solution of 0.05 to 1 weight percent of a corrosion inhibitor comprised of 1 to 9 parts by weight of an organic sulfur compound having sulfur present in the form —S— or S= and 9 to 1 parts by weight of an adduct obtained by reacting at 150 to 250°F. one mole of an ammonium derivative having at least one hydrogen atom bonded to a nitrogen atom and no other substituents reactive under the conditions of the reaction with 1.5 to 10 moles of a ketone having at least one hydrogen bonded to the carbon atom adjacent to the carbonyl group, 2 to 10 moles of an aldehyde selected from 1 to 16 carbon aliphatic aldehydes and aromatic aldehydes having no other reactive substituents and 0.3 to 24 parts by weight for each part by weight of the sum of the weights of the ammonium derivative, ketone and aldehyde, of a 1 to 20 carbon fatty acid.

14. A process as claimed in claim 13 wherein in the components for the inhibitor, the organic sulfur compound is an N-alkylthiourea, the ammonium derivative is dehydroabiethylamine, the ketone is acetophenone, the aldehyde is paraformaldehyde and the acid is formic acid.

15. A process for the removal of scale deposits containing iron oxide from the water-side surfaces of a flowing water system

oxalic acid, malonic acid, tartaric acid, formic acid, acetic acid, or sulfuric acid in place of citric acid, in Examples 1 or 2, similar eminently satisfactory cleaning results are obtained.

WHAT WE CLAIM IS:—

1. A process for the removal of scale deposits containing iron oxide and hardness as hereinbefore defined from the water-side surfaces of a flowing water system which process comprises adding one or more amino carboxylate chelating agents to the water in a proportion to dissolve substantially all of the scale, wherein substantially all of the hardness scale is removed by a first stage treatment in which the chelating agent and as required sufficient of a water soluble base is added to the water to provide a solution of from 7 pH to 12 pH and the alkaline solution is circulated for a period of time to bring the chelation reaction substantially to completion and substantially all of the iron oxide is removed by a second stage treatment in which an acidifying agent is added to the water in a proportion to provide a solution of 3 to 6 pH additional chelating agent being added as required, and the acidic solution is circulated for a period of time to bring the reaction of the solution with the iron oxide substantially to completion.

2. A process as claimed in claim 1 wherein the water in the system is substantially all displaced with make-up water prior to the first stage treatment.

3. A process as claimed in claim 1 or 2 wherein the alkaline solution of the first stage treatment is substantially all displaced with make-up water prior to the second stage treatment.

4. A process as claimed in any of claims 1 to 3 wherein the soluble base is added in a proportion to provide a first stage solution of 8 to 11 pH.

5. A process as claimed in any of claims 1 to 4 wherein the soluble base is added in a proportion to provide a first stage solution of 10 to 11 pH.

6. A process as claimed in any of claims 1 to 5 wherein the soluble base is caustic soda.

7. A process as claimed in any of claims 1 to 6 wherein the acidifying agent is added in a proportion to provide a second stage solution of 4.0 to 5.5 pH.

8. A process as claimed in any of claims 1 to 7 wherein sulfuric acid, one or more di-, tri-, or poly-carboxylic acids having 2 to 8 carbon atoms or aminopolycarboxylic acids are added to acidify the second stage solution.

9. A process as claimed in any of claims 1 to 7 wherein citric acid, tartaric acid, acetic acid or formic acid or a combination of two or more thereof is added to acidify the second stage solution.

10. A process as claimed in any of claims 1 to 9 wherein the chelating agent employed is selected from alkali metal- or ammonium salts of aminocarboxylic acids.

11. A process as claimed in any of claims 1 to 10 wherein the chelating agent employed is selected from alkali metal- or ammonium salts of aminocarboxylic acids of the formula

$$(HOOCCH_2)_2N[(CH_2)_nN(CH_2COOH)]_m\ CH_2COOH,$$

wherein n is an integer from 1 to 4 inclusive and m is a numeral in the range of 0 to 4 inclusive and wherein up to two of the carboxymethyl groups may be replaced with a β-hydroxyethyl group and one or more of the carboxymethyl groups may be replaced by carboxymethyl groups.

12. A process as claimed in any of claims 1 to 11 wherein a corrosion inhibitor is added to the acidic second stage treatment solution.

13. A process as claimed in any of claims 1 to 11 wherein corrosion in the system is substantially reduced by the presence in the acidic second stage treatment solution of 0.05 to 1 weight percent of a corrosion inhibitor comprised of 1 to 9 parts by weight of an organic sulfur compound having sulfur present in the form —S— or S= and 9 to 1 parts by weight of an adduct obtained by reacting at 150 to 250°F. one mole of an ammonium derivative having at least one hydrogen atom bonded to a nitrogen atom and no other substituents reactive under the conditions of the reaction with 1.5 to 10 moles of a ketone having at least one hydrogen bonded to the carbon atom adjacent to the carbonyl group, 2 to 10 moles of an aldehyde selected from 1 to 16 carbon aliphatic aldehydes and aromatic aldehydes having no other reactive substituents and 0.3 to 24 parts by weight for each part by weight of the sum of the weights of the ammonium derivative, ketone and aldehyde, of a 1 to 20 carbon fatty acid.

14. A process as claimed in claim 13 wherein in the components for the inhibitor, the organic sulfur compound is an N-alkylthiourea, the ammonium derivative is dehydroabiethylamine, the ketone is acetophenone, the aldehyde is paraformaldehyde and the acid is formic acid.

15. A process for the removal of scale deposits containing iron oxide from the water-side surfaces of a flowing water system

substantially as hereinbefore described with reference to Examples 1 and 2.

16. A flowing water system from which scale deposits containing iron oxide have been removed by a process claimed in any of the preceding claims.

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